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In addition to the above, also more classical experimental techniques were used. Excitation spectroscopy in the infrared showed that Er-related emission at $\lambda \approx 1.5$ μm could be induced by photons with energies significantly lower than the bandgap of Si. Finally, by magneto-optical spectroscopy symmetry of the Er-related optical center dominant MBE-grown selectively Er-doped Si structures was found to be orthorhombic. In this was microscopic information on the structure of an optically active Er-related center in Si has been obtained in the most direct way.

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Dr. hab. Tom Gregorkiewicz

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United States Army

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Abstract

Excitation and de-excitation mechanisms responsible for photoluminescence of Er^{3+} ion in crystalline silicon were investigated by a variety of experimental techniques. Special emphasis was on the two-color time-resolved spectroscopy in the mid-infrared performed at a free-electron laser facility. Application of this technique for spectroscopic investigations of energy transfers within the Si:Er system has been originally proposed and developed in the team of the Principal Investigator. This unique experimental approach revealed that optical excitation of Er^{3+} ion is a sequential two–stage process. Localization of a secondary particle, with a subsequent electron-pair recombination and energy transfer to the 4f-electron core, requires a prior capture of a primary particle by a local potential at an Er-related optically active center. Such a process is similar to exciton binding at isoelectronic centers. Consequently, optical properties of a silver dopant representing this class of defects were investigated.

In addition to the above, also more classical experimental techniques were used. Excitation spectroscopy in the infrared showed that Er-related emission at $\lambda \approx 1.5$ μm could be induced by photons with energies significantly lower than the bandgap of Si. Finally, by magneto-optical spectroscopy symmetry of the Er-related optical center dominant MBE-grown selectively Er-doped Si structures was found to be orthorhombic. In this was microscopic information on the structure of an optically active Er-related center in Si has been obtained in the most direct way.

Key words

photoluminescence, excitation spectroscopy, silicon photonics, energy transfers, non-radiative recombinations, Rare-Earth doping, excitons, impurities

Table of contents

List of participating scientific personnel

1. Drs M. Forcales – Ph.D. student, University of Amsterdam
2. Drs M.A.J. Klik – Ph.D. student, University of Amsterdam
3. Drs N.Q. Vinh – Ph.D. student, University of Amsterdam

1. INTRODUCTION

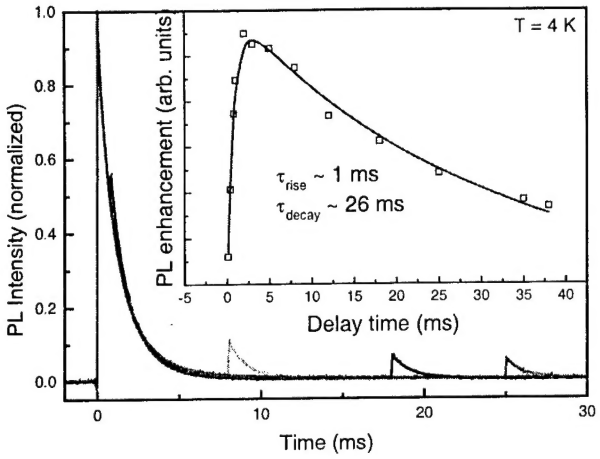
Due to the indirect character of its (relatively small) energy gap between the valence and the conduction bands, optical properties of silicon appear rather uninteresting and, as such, are not very well investigated. Among various attempted methods for improving the photonic potential of this most important electronic material, "optical" doping with Rare Earth (RE) ions is currently recognized as the most successful approach. From a variety of explored dopants, Er ions attract the most attention since their characteristic emission at $\lambda \approx 1.5$ μm coincides with the absorption minimum of glass fibers commonly used in nowadays communication networks. Yet the excitation mechanisms responsible for the energy transfer between the silicon matrix and the highly localized 4f-electron shell of the RE ion are very complex. Their detailed understanding is the necessary prerequisite for development of efficient room-temperature operating devices. Similarly, construction of the highly-desired all-silicon Si:Er-based laser requires a comprehensive understanding of the excitation path from the silicon matrix to the 4f-electron core of Er ion, allowing for its optimization by materials engineering. In particular, for the future of Si:Er-based photonic devices it is necessary to explain why under optical pumping the excitation mechanism saturates before population inversion occurs, so that the stimulated emission regime cannot be reached. An equally important task is the search for alternative excitation mechanisms that could eventually lead to the population inversion and superluminescence and, upon further development, to laser action.

In the current project we investigate energy transfer mechanisms in optically excited Si:Er system. We take a full advantage of a novel experimental approach of the two-color spectroscopy in the mid-infrared (MIR), making use of a free-electron laser (FEL). We also look, to our knowledge for the first time, at the excitation spectrum of Er^{3+} ion in Si. In a specially developed unique Si/Si:Er superlattice structure we investigate the micro-structure of the dominant Er-related optically active center. Finally, recognizing that the electronic structure of Er dopant in crystalline silicon bears many similarities to that of an isoelectronic center, we present time-resolved photoluminescence data for a prominent representative of this class of defects – a silver dopant embedded in crystalline Si.

In what follows a brief description of the main results obtained for each of the above-mentioned specific research subjects is presented, followed by a list of relevant publications prepared within the project period.

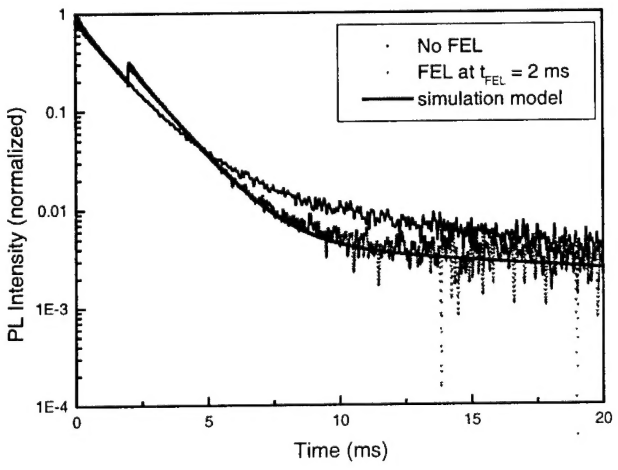
1. MIR-ACTIVATED EMISSION

For Si:Er system band-to-band excitation of the host results in an energy transfer to the 4f core of Er^{3+} ions and gives rise to the characteristic emission at $\lambda \approx 1.5$ μm. We have found out that excitation of Er^{3+} ions embedded into crystalline silicon can be accomplished in the mid-infrared with photons of 70-170 meV. These energies are several times smaller than that of the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition. The intensity of Er-related emission at 1.54 μm was shown to enhance upon application of a MIR pulse from a free electron laser (FEL). The effect was found to take place when the MIR pulse was applied within a short delay time after band-to-band excitation of the sample by a short pulse from a Nd:YAG laser operating in the visible. The enhancement disappeared with a relatively large time constant τ_D of several tens of milliseconds.



The MIR-induced enhancement of the Er PL is illustrated in the figure. In the experiments, performed at the Dutch free-electron laser user facility (FELIX), the sample (in the depicted case Er-implanted Cz-Si, co-implanted with oxygen, and annealed at 900°C for 30 minutes), is initially excited with a nanosecond pulse of the second harmonic of the Nd:YAG laser at λ_{YAG} = 532 nm. A MIR pulse from the FEL is applied with a millisecond delay with respect to the pump pulse and induces an additional PL signal. The wavelength and the characteristic decay time uniquely identify the FEL-generated PL as originating from the same Er-related optical centers that can also be excited by the visible laser pulse. As illustrated by the inset to the figure, the magnitude of the effect depends on the Δt delay time of the MIR pulse. The initially observed "incubation" time of the enhancement is related to saturation of Er and does not occur for a low intensity of primary excitation.

In a comprehensive treatise, recombination of carriers (temporarily) stored at shallow levels following the band-to-band excitation, was identified as the mechanism responsible for the MIR-activated Er PL. By scanning the wavelength of the MIR beam, ionization energies E_i of traps responsible for carrier storage were determined. It was established that E_i and τ_D values were influenced by sample parameters. Based on detailed time-resolved investigations, we linked the enhancement effect to a slowly decaying component commonly appearing in the kinetics of the Si:Er PL signal. A model was developed where the intensity enhancement is ascribed to the MIR-induced energy transfer from shallow traps to Er^{3+} ions. Using this model we can successfully describe the amplitude of the FEL-induced effect for different time delays – see figure below.



Based on the study, we developed a complete model of the low-temperature kinetics of Er-related emission in crystalline Si. The "slow" component with the sample-dependent time constant of tens of milliseconds is attributed to excitation of Er ions by thermal emission from non-equilibrium traps. These traps are populated by the Nd:YAG pump pulse and thermally emit carriers while returning to equilibrium. Their recombination leads to excitation of Er ions. Since the

time constant of thermal emission exceeds the Er relaxation time, this "slow" excitation process is directly reproduced in the kinetics of the Er-related PL signal. Alternatively, carriers localized at these traps can be rapidly ionized by the FEL, resulting in an abrupt increase of the Er PL. This explanation is additionally supported by temperature dependence of the MIR-induced enhancement effect: as temperature increases, thermal emission from traps becomes more efficient and the FEL-induced enhancement effect disappears.

Relevant papers prepared within the project period

APS journals

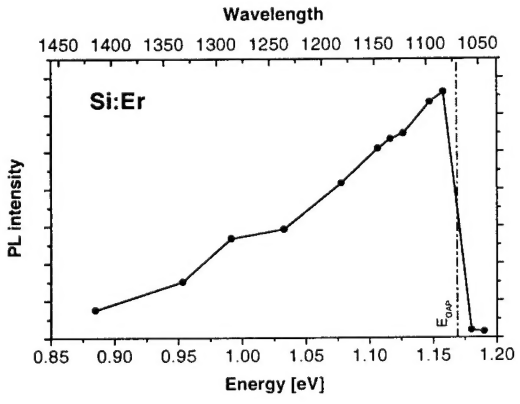
1. T. Gregorkiewicz, D.T.X. Thao, J.M. Langer, H.H.P.Th. Bekman, M.S. Bresler, J. Michel, and L.C. Kimerling, *"Energy transfer between shallow centers and RE ion core: Er^{3+} ion in silicon"*, Phys. Rev. B **61**, 5369-5375 (2000)
2. O.B. Gusev, M.S. Bresler, P.E. Pak, I.N. Yassievich, M. Forcales, N.Q. Vinh, and T. Gregorkiewicz, *"Excitation cross-section of erbium in semiconductor matrices under optical pumping"*, Phys. Rev. B **64,** 075302, (2001)..

Other journals

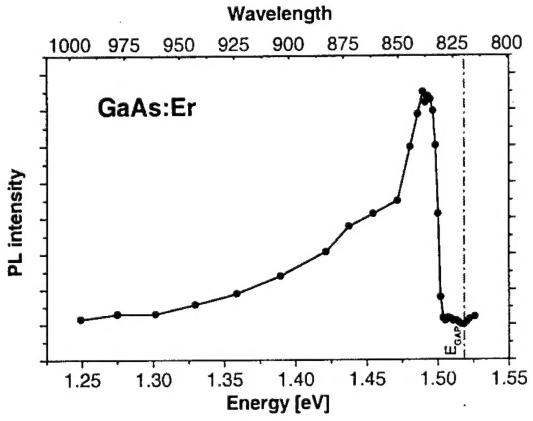
3. T. Gregorkiewicz, D.T.X. Thao, J.M. Langer, and H.H.P.Th. Bekman, *"Tracking recombination processes in Si:Er with a free-electron laser"*, J. Lumin. **87-89**, 96-100 (2000).
4. M. Forcales, I.V. Bradley, J-P.R. Wells, and T. Gregorkiewicz, *"Mid-infrared induced quenching of photoluminescence in Si:Er"*, Mater. Sci. Eng. B **81**, 80-82 (2001).
5. J.M. Langer and T. Gregorkiewicz, *"Rare-Earth impurities in semiconductors"*, to appear in Encyclopedia of Materials Science and Technology, K.H.J. Buschow (ed.), Pergamon Press (2001).
6. M. Forcales, I.V. Bradley, J-P.R. Wells, and T. Gregorkiewicz, *"Time-resolved investigation of the mid-infrared induced enhancement of Er^{3+} emission in Si"*, to appear in Physica (2001).
7. M. Forcales, I.V. Bradley, J-P.R. Wells, and T. Gregorkiewicz, *"Temporal characteristics of the optical storage effect in Si:Er"*, to appear in Mater. Sci. Eng. B (2001).
8. M. Forcales, M. Klik, N.Q. Vinh, I.V. Bradley, J-P.R. Wells, and T. Gregorkiewicz, *"Free-electron laser studies of energy transfer mechanisms in semiconductors doped with Transition Series ions"*, to appear in J. Lumin (2001).

2. SUBBANDGAP EXCITATION

It is well known that the Er^{3+} ion can form a variety of complexes in the Si host material, most probably each with its own level within the bandgap. Excitation spectroscopy is a powerful method to investigate these levels and their role in the excitation process. Using an OPO laser system, we have performed pulsed excitation experiments in a wavelength range of 700-2200 nm on an MBE-grown oxygen rich Si:Er layer of 1.8 μm and, for comparison, on an MBE-grown GaAs:Er sample.



After excitation of the sample from the substrate side with the OPO beam operating in the near infrared, a PL signal at $\lambda \approx 1.54$ μm, originating from the intra-4f-shell transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of the Er^{3+} ion could be detected. In the figure, the photoluminescence excitation (PLE) spectrum measured for 1539 nm at a temperature of 10 K is shown.



The simultaneously monitored photon flux of the OPO-beam shows a monotonous behavior in the depicted wavelength range. It is clear from the data that the Er-related luminescence can be observed for excitation photon energies between the bandgap energy E_g of the silicon host and the energy of the intra-4f-shell transition. The cross section for excitation decreases monotonically with smaller photon energy and vanishes for energies below this transition. No resonant features are present in the investigated range of 1125 - 2200 nm. Although multi-photon absorption seems an obvious explanation for the observed excitation spectrum, the dependence of PL intensity on OPO-beam power shows a completely linear behavior, indicating other processes to be responsible for the excitation of the RE-ion with sub-bandgap photon-energies. At the same time, the structure of the PL spectrum is independent of the excitation wavelength showing that the emission is always due to the same Er-related optically active centers.

At present, the observations cannot be explained by any of the (so far) considered excitation models. For a better understanding of responsible excitation processes, further investigations are necessary on a variety of samples and in different experimental configurations. These will be performed shortly.

For comparison, the PLE spectrum for MBE grown GaAs:Er was obtained using the same experimental setup. Also in this case Er-related PL could be obtained with subband energies, but only for excitation wavelengths below 1000 nm.

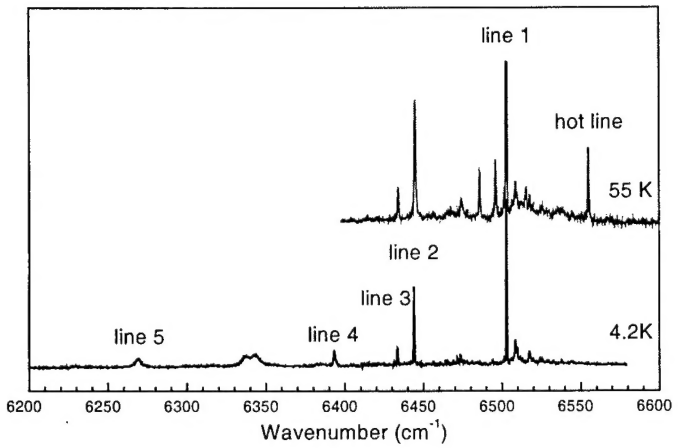
Relevant papers prepared within the project period

Other journals

1. M.A.J. Klik and T. Gregorkiewicz, *"Excitation of Si:Er with sub-bandgap energies"*, Proceedings of ICDS-21, to appear in Physica (2001).

3. MICROSTRUCTURE OF THE DOMINANT OPTICALLY ACTIVE Er-RELATED CENTER

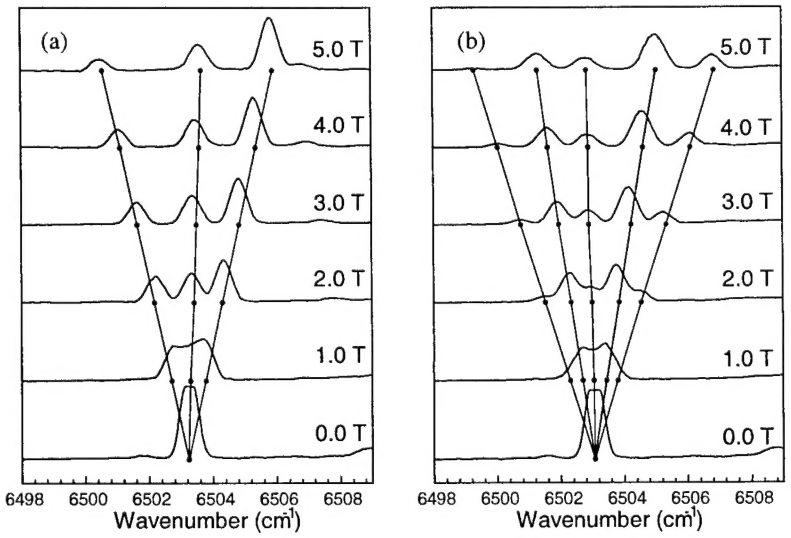
Determination of the microstructure of the dominant optical center formed by Er doping in crystalline silicon is of prime importance for successful development of efficient emitters based on Si:Er. The situation is complicated due to a multiplicity of Er-related centers; more than 100 emission lines have been identified in a high-resolution infrared absorption study on Er-implanted Si and assigned to emissions from several, simultaneously present Er-related centers. On the other hand, prominent formation of a cubic symmetry center (an isolated Er ion at a tetrahedral interstitial site) was shown by channeling experiments. The channeling studies could not, however, conclude on optical activity of such an isolated Er interstitial. Also electron paramagnetic resonance was not successful in identification of optically active Er-related centers in Si. Similarly, attempts to observe the Zeeman effect in PL of Si:Er were disappointing. Due to inhomogeneous



character of the linewidth induced by the earlier mentioned multiplicity of spectral components, application of magnetic field results in broadening, and subsequent vanishing of emission lines.

Recently, sublimation MBE technique offered new possibilities to develop high quality Si:Er structures. Figure above shows PL spectrum of a quantum structure of 400 interchanged Si and Si:Er nano-layers prepared by this technique. PL emission from such a sample is by at least an order of magnitude more intense than for implanted Si:Er and contains only a few lines of a very small width (~ 10 μeV).

Taking advantage of the narrow linewidth, we were able to report for the first time a successful observation of the Zeeman effect in luminescence of a crystalline Si:Er structure. A clearly resolved splitting of major spectral components was observed in magnetic fields up to 5.5 T. The figure below shows the magnetic field-induced splitting of the strongest PL line (marked 1 in the spectrum) for (a): **B**||<100> and (b): **B**||<011> configurations. As can be seen, line 1 splits in the magnetic field into 3 components for **B**||<100> and 5 components for **B**||<011>. For both field orientations, position of one of them remains almost independent of the magnetic field – in this case the effective g-factors of the upper and the lower states must be nearly equal. Assuming that all lines stem from one type of center, and that there is no accidental overlap of PL lines from centers of different symmetry at **B**=0, we have to consider a low symmetry center with different orientations of the g-tensor axes of the possible configurations in respect to **B** direction.



The observed splitting corresponds very well to the orthorhombic I (C_{2v}) symmetry type. The number of lines agrees with this symmetry type, and their relative intensities reflect the expected ratios of 2:1 for **B**||<100> and 1:4:1 for **B**||<011>.

Based on the preliminary analysis of the Zeeman effect data, we conclude that the individual components of the Er PL spectrum originate from more than one type of Er-related optically active centers. The symmetry of the most prominent center is tentatively identified as orthorhombic I (C_{2v}). At least one spectral component corresponds to an Er-related center of cubic symmetry. All the observed PL lines are due to electric dipole-induced transitions without spin flips. Therefore precise determination of the ground-state g-tensor is at this moment not possible.

In the continuation of the project, currently under way, we will investigate Zeeman effect for an arbitrary field orientation, i.e. not along the main directions, where also circularly polarized $\Delta M_J = \pm 1$ transitions should appear. In a higher temperature range T>30K, we will look carefully at the intensity changes of individual components as induced both by temperature and field increase. In that way we hope to obtain independent information on Zeeman effect for the excited state, allowing for an unambiguous determination of g-tensors. Also the polarization effects will be carefully investigated. As a result, a microscopic model of the Er-related center optically active in the MBE-grown structure will be developed.

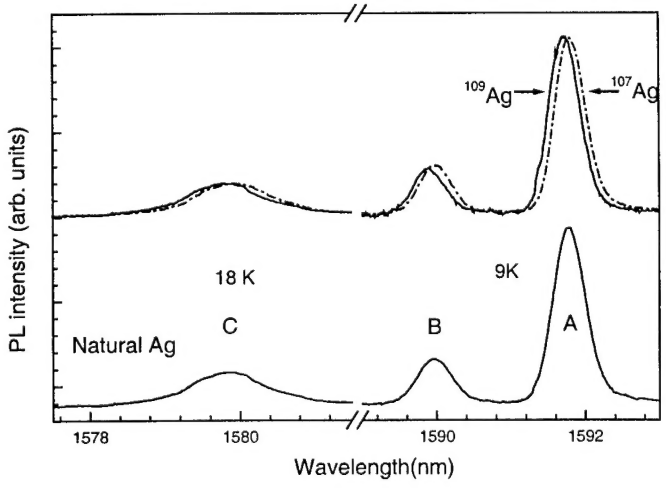
Relevant papers prepared within the project period

Other journals

1. N.Q. Vinh, H. Przybylińska, Z.F. Krasil'nik, B.A. Andreev, and T. Gregorkiewicz, *"Observation of Zeeman effect in photoluminescence of Er^{3+} ion in crystalline silicon"*, Proceedings of ICDS-21, to appear in Physica (2001).

4. RECOMBINATION OF EXCITONS BOUND TO ISOELECTRONIC CENERS IN Si

Like other noble metals, silver is an important dopant of silicon due to its interesting physical properties and possible applications for device manufacturing. It has an isoelectronic character and, when introduced into silicon, gives rise to an acceptor (E_{CB}-0.54 eV) and a donor level (E_{VB}+0.34 eV). In photoluminescence, silver-doped silicon exhibits a characteristic emission band at 780 meV. This band consists of narrow no-phonon lines (termed A, B, C at energies 778.91, 779.85 and 784.31 meV, respectively) which are replicated at lower energies by local phonons. The structure of the 780 meV band was identified as transitions from the effective-mass-theory electronic states near the conduction band to the ground state.



In the present project, the A-B-C photoluminescence band at 780 meV, previously assigned to silver-related

centers in Si on basis of sample production conditions, was investigated in detail. For that purpose we prepared special samples doped with isotopically enriched silver. With high-resolution PL spectroscopy, we were able to observe the silver isotope shift of the components of the 780-meV band. We observed isotope shift of the three main no-phonon A, B, and C lines. The effect is illustrated in the figure below, where the PL spectrum of the A-B-C band for silicon doped with natural and isotopically enriched silver is compared. A clear shift (of approximately 35 μeV between the ^{107}Ag and the ^{109}Ag doping) is evident. Observation of this effect conclusively shows that silver is incorporated in the microscopic structure of the luminescent defect.

We have also investigated decay kinetics of the 780 meV band. From time-resolved PL lifetimes of an order of 100 μs were determined. The long lifetimes of the three dominant no-phonon lines of the 780 meV band are in agreement with a model of radiative recombination of an exciton localized at an isoelectronic center. Further insight in the nature of the optically active Ag-related center was obtained from the temperature dependence of the lifetime.

Relevant papers prepared within the project period

APS journals

1. N.Q. Vinh, K. Thonke, and T. Gregorkiewicz, *"780 meV photoluminescence band in silver-doped silicon: Isotope effect and time-resolved spectroscopy"*, to appear in Phys. Rev. B (2002).

Other journals

2. N.Q. Vinh, M.A.J. Klik, and T. Gregorkiewicz, *"Time-resolved photoluminescence study of Si:Ag"*, Proceedings of ICDS-21, to appear in Physica (2001).

5. CONCLUSION

In addition to the immediate experimental results of the individual research tasks summarized in relevant sections, also a more general conclusion concerning the optical excitation mechanism of Er^{3+} ion in crystalline silicon has been obtained within the project. While it is generally acknowledged that exciton recombination plays a prominent role in this process, current findings shed new light on the microscopic mechanism of the electron-hole recombination responsible for the Er core excitation. Based on the results from the two-color spectroscopy in the MIR, we conclude that localization of an electron-hole pair by an individual Er-related optical center takes place in two stages. Similar to the exciton binding by isoelectronic centers, first a primary particle (in this case most probably a hole) is captured by a local potential. Following that, a secondary particle (most probably electron) is bound in a long-range potential of a localized hole. As clearly shown by the time-resolved experiments, these two stages can be separated in time by as much as several hundreds of milliseconds.

This conclusion opens new possibilities of the so far unexplored excitation schemes for the Si:Er system, where in the first stage a sample would be "prepared" for excitation by pumping with a single type of carriers only. Er core excitation would be then accomplished in a second and final stage, upon injection of carriers of the opposite type.

Future research should explore whether by careful tuning of this new excitation scheme population inversion within the notorious Si:Er system can be reached, paving way for development of efficient light-emitting sources based on Si:Er.